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Deposition of thin polycrystalline films of cuprous thiocyanate on conducting glass and photoelectrochemical dye-sensitization

K. Tennakone, A.R. Kumarasinghe, P.M. Sirimanne, G.R.R.A. Kumara

Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka Received 12 October 1994; accepted 17 January 1995

Abstract

A method is given for electrochemical deposition of thin polycrystalline films of cuprous thiocyanate (p-type semiconductor, band gap = 3.6 eV) on conducting indium-tin oxide glass. Dye-sensitization of the surface with methyl violet and construction of a photoelectrochemical cell are described. The investigation demonstrates the usefulness of unconventional high band gap semiconductors in studying dye-sensitization.

Keywords: Copper; Deposition process; Solar cells

1. Introduction

Dye-sensitization of thin films of semiconductor surfaces and their utilization in photoelectrochemical cells (PECs) have attracted a great deal of attention [1-5]. An important contribution in this direction is the observation by Gratzel and co-workers that dye-sensitized PECs based on colloidal films of TiO₂ possess the ability to convert solar energy at practically viable efficiencies [6-8]. It is likely that similar or better cells of this type could be made with colloidal films of other semiconducting materials. A major problem in the study of dye-sensitization is the enhancement of the absorption of the dve at the semiconductor surface and the prevention of the subsequent leaching of the adsorbed dye into the solution. Dye-sensitization affords a way of extending the spectral response of stable wide band gap semiconductors to the visible spectrum. However, familiar dyes are poorly adsorbed on the surfaces of most conventional high band gap semiconductors (e.g. TiO_2).

In a series of reports, one of the present authors (KT) and other collaborators have discussed the properties of the unconventional semiconductor CuCNS (cuprous thiocyanate) and the suitability of thin films of this material for making dye-sensitized PECs [9–11]. Solid CuCNS exists in two polymorphic forms (α and β), the common β -form is a three-dimensional polymer composed of layers of close-packed CuCNS units [12–15]. As a result of the polymeric nature of β -CuCNS, thin films of CuCNS are largely free from cracks and pin-holes [10,11]. The other important property of CuCNS is that it readily adsorbs cationic dyes, whose anionic component is CNS⁻[9]. The mechanism of adsorption is presumably the formation of a solid-solution thiocyanate of the cationic dye and CuCNS. This is supported by the observation that CuCNS is soluble in a saturated solution of the thiocyanated dye or the molten dye. The β -form of CuCNS in the absence of impurities behaves as a p-type semiconductor of band gap ≈ 3.6 eV [10].

In our earlier reports [9-11], we discussed the deposition of CuCNS on a copper substrate by chemical or electrochemical methods. Deposits on copper substrates are contaminated with oxides of copper and a stoichiometric excess of copper is also introduced [10]. In this work, we describe a method for deposition of pure CuCNS on conducting tin oxide-coated glass and construction of a dye-sensitized PEC.

2. Experimental

All chemicals used, ie KCNS, KI, I_2 , CuSO₄ and ethanol were of analytical grade. Indium-tin oxide

(ITO) glass plates $(1 \times 3 \text{ cm} \text{ linear dimensions and})$ sheet resistance $\sim 10 \Omega$) were washed with NaOH (0.05 M) followed by dil HCl (0.05 M), distilled water and dried. The solution for electrochemical coating of CuCNS was prepared as follows: 1.0 g of ground CuSO₄ is mixed with 1.5 g of ground KCNS and the mixture is agitated in 5 ml of ethyl acetate. Dark-brown coloured Cu(CNS)₂ formed as a result of the double-decomposition reaction between CuSO₄ and KCNS gets dissolved in ethyl acetate. After separation of the solid residue, 1 ml of this solution and 2 ml of cupric acetate or propionate $(6 \times 10^{-2} \text{ M})$ are mixed with 30 ml of 99% ethanol. Cupric acetate or propionate are used as they are copper salts soluble in ethanol and free of interfering anions (for example copper (II) chloride cannot be used as Cl⁻ interferes with the deposition of CuCNS). To increase the conductivity a few drops of water is also added (fully aqueous solution cannot be use owing to the instability of $Cu(CNS)_2$ in water). The solution was electrolysed with a ITO glass plate as the cathode and a platinum mesh as the counter electrode. The current density was galvanostatically controlled at ~ 0.8 mA cm⁻² (Hukuto Denko HA 301 potentiostat). CuCNS gets deposited on the cathode via the reaction

$$Cu(CNS)_2 + e^- \rightarrow CuCNS + CNS^-$$
(1)

An increase in copper (II) ion concentration relative to CNS^- enhances the formation of the deposit. Cupric acetate or propionate was included in the coating solution for this purpose. The exact mechanism responsible for this effect is not clear. Perhaps combination of CNS^- ions generated in reaction (1) with Cu^{2+} prevents the depletion of $Cu(CNS)_2$ concentration near the surface of the cathode. The thickness of the film was calculated on the basis of reaction (1), noting the duration of electrolysis and from the knowledge of the density of CuCNS.

The dye used for sensitization was methyl violet, which is commercially available in the chloride form. Thiocyanate of the form of the dye was made by the following method. The dye (chloride) was digested with a hot saturated solution of KCNS for ~ 45 min. As a result of the double-decomposition reaction

$$DCl + KCNS \rightarrow KCl + DCNS$$
 (2)

where D denotes the dye, the less soluble thiocyanate form of the dye (DCNS) separates on cooling the solution. The pure thiocynated form of the dye can be recrystallized after extraction with alcohol. CuCNScoated ITO glass plates are dyed by keeping then immersed in an aqueous solution of the thiocyanate of the dye. The surface density of absorption depends on the concentration of the dye solution and the duration of immersion. The amount of dye adsorbed was determined by extraction with ethanol and spectroscopic estimation.



Fig. 1. Photocurrent action spectrum (curve a) and the absorption spectrum (curve b) of the methyl violet-sensitized CuCNS photo-cathode.

A PEC was constructed with a dye-coated CuCNS/ ITO plate as the photocathode and a platinum mesh as the counter electrode. The electrolyte used was KI containing I_2 . In all experiments, the photocathode was biased at 0.13 V vs. SCE (standard calomel electrode) which gave zero dark voltage for the cell. The stability of the cell was monitored under illumination with a 60 W tungsten filament lamp. A Nikon Monochromator Auto-Scanner As-C-101 recorded the photocurrent action spectra, after amplification in a lock-in system. The variation of the photocurrent at the peak wavelength in the action spectrum was investigated using the same experimental set-up.

3. Results and discussion

Electrolysis for 3 min under the conditions described in the experimental section gave a CuCNS film of thickness ~1.3 μ m. Deposition at high current density yields films consisting of fine crystallites, such films give higher photocurrents and readily reproducible results. The film was resistant dilute mineral acids. The photoresponse of the dye-coated plate was largely independent of the film thickness provided, full coverage is obtained. Fig. 1 compares the photocurrent action spectrum of the cell with absorption spectrum of the dye (methyl violet). It is seen that the action spectrum is similar to the absorption spectrum, but a red-shift in the former is observed. The presence of the red-shift is an indication that only adsorbed dye molecules are effective in generating the photocurrent.

Cathodic dye-sensitization occurs when the excited dye adsorbed at the CuCNS surface injects holes into the conduction band. Reactions at the electrode surfaces can be summarized as follows.



Fig. 2. Variation of the photocurrent with I_2 concentration in the electrolyte, when the cathode is illuminated with monochromatic light at a peak wavelength 630 nm in the action spectrum.





Fig. 3. Time development of the photocurrent when the cell is illuminated with a 60 W tungsten filament lamp.

1. Photocathode

 $D + hv \to D^* \tag{3}$

$$D^* \rightarrow D + h^+$$
 (4)
 \downarrow
valance band

 $2D^{-} + I_{3}^{-} \to 3I^{-} + 2D \tag{5}$

Here D^* is the excited dye molecule that injects a hole into the valence band (h⁺) of CuCNS forming the dye an- ion D , which transfers an electron to I_3 to regenerate the dye.



Fig. 4. Variation of the photocurrent (measured at the peak wavelength 630 nm) with the surface concentration (SC) of the dye.



Fig. 5. Structural formula of methyl violet.

2. Anode

I

lodide ions donate electrons to the anode, giving iodine which combines with I to produce I_3 , i.e.

$$2\mathbf{I}^- - 2\mathbf{e}^- \to \mathbf{I}_2 \tag{6}$$

$$^{+}+\mathbf{I}_{2}\rightarrow\mathbf{I}_{3}^{-}$$
 (7)

The photocurrent depends on the equilibrium concentration of I $_$ and I₃ $_$. Fig. 2 shows the variation of the photocurrent at the peak wavelength (630 nm) with the I₂ concentration in the solution. It is seen that, initially, the photocurrent increases with the increase of I₂ and thereafter a saturation is reached.

The time development of the photocurrent under illumination with a 60 W tungsten filament lamp is shown in Fig. 3. A slight ($\sim 5\%$) decrease in the photocurrent is noticeable after ~ 1 h. As fading of the dye is also observed, the decay of the photocurrent is

caused by photodegradation of the dye. Fig. 4 shows the rent obtainable from the cell was found to depend on surface concentration (SC) of the dye. Fig. 4 shows the variation of the photocurrent at peak wavelength (630 nm) with SC of the dye. At low SCs, the light absorption cross-section is small, however as SC is increased the probability of de-excitation of excited dye molecules by mutual interaction concentration quenching) increases, thereby (i.e. decreasing the photocurrent. Thus there is a optimum dye SC and from the data of Fig. 4 we obtain $[SC]_{op} \approx 8 \times 10^{14}$ molecules cm⁻². The monolayer thickness coverage estimated from dimensions of the methyl violet molecule (Fig. 5) is $\sim 1 \times 10^{14}$ cm^{-2} . Thus the maximum photocurrent is obtained when the surface coverage is a few monolayers. (i.e. the surface density of $[SC]_{op}$ is equivalent to ~8 monolayers). We believe that, just as in the case of the Gratzel cell, the photocurrent can be enhanced by several orders of magnitude if colloidal films of CuCNS are adopted.

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